

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08K 5/07, C08L 67/08, C08G 63/91</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/41833</b> <b>(43) International Publication Date:</b> 27 December 1996 (27.12.96)
<b>(21) International Application Number:</b> PCT/NL96/00221 <b>(22) International Filing Date:</b> 5 June 1996 (05.06.96) <b>(30) Priority Data:</b> 1000534 9 June 1995 (09.06.95) NL <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> HENDRIKS, Johannes, Wilhelmus, Maria [NL/NL]; Van Echtenmarke 4, NL-8016 DB Zwolle (NL). <b>(74) Agent:</b> SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BB, BG, BR, CA, CN, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> BINDER COMPOSITION COMPRISING A STRONGLY ACTIVATED CARBANION-FUNCTIONAL POLYMER AND A CROSS-LINKER  <b>(57) Abstract</b>  The invention relates to a binder composition comprising a strongly activated carbanion-functional polymer and a cross-linker. The cross-linker contains aldehyde groups and the polymer is an alkyd resin or a polyester resin. The carbon-functional groups are acetoacetate groups, malonate groups, acetate groups or mixtures thereof. Preferably, the polymer is an alkyd resin having said carbanion-functional groups and having a hydroxyl number between 40 and 70 mg of KOH/gram of resin and an acid number between 15 and 25 mg of KOH/gram of resin.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

5     BINDER COMPOSITION COMPRISING A STRONGLY ACTIVATED  
      CARBANION-FUNCTIONAL POLYMER AND A CROSSLINKER

10     The invention relates to a binder composition comprising a strongly activated carbanion-functional polymer and a crosslinker.

15     A binder composition of this type is disclosed in EP-A-227454. In this disclosure an acetoacetate-modified polymer is crosslinked with use of a Michael addition reaction with poly- $\alpha,\beta$ -unsaturated esters. Binder compositions which are cured by means of Michael addition reactions generally yields coatings that are slow drying and unacceptably yellow.

20     One object of the invention is to provide binder compositions comprising a strongly activated carbanion-functional polymer, especially an alkyd resin or a polyester resin, and a crosslinker that quickly dry.

25     The invention is characterized in that the crosslinker contains aldehyde groups.

      In this way quicker drying of binder compositions comprising a strongly activated carbanion-functional polymer is achieved.

30     It is another advantage of the present invention that coatings based on binder compositions according to the invention show less yellowing.

      Preferably, the aldehydes have (1-20) carbon atoms.

35     Generally the crosslinker contains aldehydes having (1-4) aldehyde groups, more preferably (1-2) aldehyde groups.

      Examples of suitable aldehydes include formaldehyde, cinnamaldehyde and polyaldehydes, such as for instance, glutardialdehyde.

- 2 -

Preferably, a mixture of formaldehyde and glutardialdehyde is used. The molar ratio of formaldehyde to glutardialdehyde can be, for example, between about 70:30 and about 30:70 and preferably, between about 55:45 and about 45:55.

A strongly activated carbanion-functional polymer is understood to be a polymer backbone modified with one or more strongly, for example, doubly, activated carbanion groups.

In theory, many polymers can serve as polymer backbone. Examples of suitable polymer matrices include alkyd resins, polyesters, polyethers and epoxy-functional resins or mixtures hereof.

Preferably, the polymer backbone comprises a polyester resin or an alkyd resin. These polymer matrices can comprise mixtures of polymers. Preferably they contain more than 50% by weight of a polyester or an alkyd resin.

Preferably, the alkyd resin has, after transesterification with the strongly activated carbanion groups, a hydroxyl number between about 40 and about 70 mg of KOH/gram of resin and an acid number of between 15 and 25 mg of KOH/gram of resin. Alkyd resins can be obtained from polyols, dicarboxylic acids or dicarboxylic acid derivatives and fatty acids, as described in, for example, EP-A-227454, the complete disclosure of which is incorporated by reference.

Preferably, unsaturated fatty acids, such as for example, tall oil fatty acid (TOFA) and soy oil fatty acid (SOFA), are incorporated into the alkyd resin.

Examples of suitable dicarboxylic acids or dicarboxylic acid derivatives include phthalic anhydride, maleic anhydride and corresponding dicarboxylic acids thereof.

Examples of suitable polyols include trimethylol propane, trimethylol ethane, cyclohexane

- 3 -

dimethanol, 1,6-hexanediol, hexane-2,5-diol, neopentyl glycol, ethylene glycol, diethylene glycol, propylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, mono- or disorbitol, mono- or dipentaerythritol, 5 trishydroxyethylisocyanurate, glycerol, polypropylene glycol, polyethylene glycol and polytetrahydrofuran.

Preferred suitable strongly activated carbanion groups include acetoacetate groups, malonate groups and acetate groups.

10 Preferably, acetoacetate groups are used such as methyl acetoacetate, ethyl acetoacetate, isopropyl acetoacetate, butyl acetoacetate, t-butyl acetoacetate, methyl benzyl acetoacetate and/or dodecyl acetoacetate.

The transesterification reaction of the 15 acetoacetate groups on the polymer can take place under usual conditions as described in, for example, EP-A-227454. The catalyst for this reaction can be for example p-toluene sulphonic acid.

The amount of strongly activated carbanion 20 groups incorporated into the polymer can be for example between about 5 and about 15 wt.%, relative to the modified polymer.

In general, the molar ratio of the carbanion groups to the aldehyde groups is between about 1:5 and 25 about 5:1, and preferably between about 1:1 and about 3:1 and more preferably between about 1:1 and about 2:1.

The binder composition according to the invention is preferably used in an aqueous emulsion 30 because binder compositions comprising a strongly activated carbanion-functional polymer and a crosslinker may form a gel in an organic solution. Moreover, the presence of solvents is undesirable in view of current environmental requirements.

35 The strongly activated carbanion-functional polymer can be emulsified in water by addition of an emulsifier and/or by neutralization of the acid groups

- 4 -

in the alkyd resin. In general, the polymer is emulsified at temperatures of between about 0°C and about 100°C, preferably at a temperature of between about 25°C and about 75°C.

5           According to a further preferred embodiment of the invention the emulsifying temperature is between about 58°C and about 62°C.

          In general the particle size of the emulsion is between 100 and 1000 nm, preferably between 200 and  
10   600 nm.

          An aldehyde compound can subsequently be added to the strongly activated carbanion-functional polymer at for example room temperature as a crosslinker.

15           The binder compositions according to the present invention can be used, for example, as a one-component system for coatings that cure at temperatures between about 0°C and about 100°C, preferably for coatings that cure at about 25°C or room temperature.

20           The binder compositions according to the present invention can be mixed with the usual additives to obtain coatings. Examples of these additives include pigments, colorants, fillers, thickeners, flow-promoting agents, matting agents, stabilizers and/or  
25   siccatives.

          The substrate material to be coated is not particularly limited but exemplary substrates include glass, plastic, wood and metal substrates.

          The invention will be explained further by  
30   reference to the following, non-limiting experiments and examples.

#### Examples

##### 35   Experiment I

Preparation of an alkyd resin with incorporated acetoacetate groups

- 5 -

1399 parts by weight of tall oil fatty acid, 857 parts by weight of phthalic anhydride and 744 parts by weight of pentaerythritol were mixed and reacted at 240 °C until a resin with an acid number of about 20 mg of KOH/gram of resin was obtained. The mixture was cooled to 160°C, 530 parts by weight of methylacetoacetate were added and methanol was distilled off for 2 hours. After the transesterification had been finished all volatile components were distilled off in a vacuum.

The characteristics of this resin are given in Table 1.

#### 15 Comparative Experiment A

##### Preparation of an alkyd resin without acetoacetate groups

1238 parts by weight of tall oil fatty acid, 1107 parts by weight of phthalic anhydride and 655 parts by weight of glycerol were reacted at 220°C until the acid number was 20 mg KOH/gram resin. The characterization of this resin is given in Table 1.

25 TABLE 1

	Alkyd resin according to Experiment I	Alkyd resin according to Experiment A
Acid number <sup>1)</sup>	22.6	20.4
Viscosity <sup>2)</sup>	0.7 dPa.s	2.7 dPa.s
Alkyd constant	0.981	0.981
% Acetoacetate groups	11.2	-
Oil length	46.5%	46.5%
OH number	62	60

1) mg KOH/gram resin

35 2) Resin diluted 1:1 in Xylene, 23°C.



- 6 -

Experiment II-III and Comparative Experiment B  
Preparation of resin emulsions

The resin emulsions are obtained by adding water very slowly to the resin/emulsifier/neutralizer mixture at a temperature of about 60°C in a ratio as illustrated in Table 2.

Table 2

10

15

20

	II	B	III
	based on alkyd resin according to Exp. I	based on alkyd resin according to Exp. A	based on a 1:1 mixture of alkyd resins according to Exp. I and A
Resin <sup>1)</sup>	1000	1000	1000
Nonylphenol-20-ethylene oxide <sup>1)</sup>	150	150	150
NaOH, 10% <sup>1)</sup>	71	120	96
Water <sup>1)</sup>	650	606	628
Physical characteristics			
d <sub>90</sub> (nm)	326	388	377
pH	5.6	5.6	5.9
% SC <sup>2)</sup>	54.6	54.6	54.6

1) Parts by weight

2) % SC = solids content

25

The particle size (d<sub>90</sub>) of the emulsion was measured with the aid of a Coulter LS-130 apparatus.

Examples

30 Preparation of a binder composition comprising formaldehyde

2.5% by weight of a drier (Siccatol 938™ from Acros), and 5% by weight of a thickener (RM 1020™, Röhm & Haas) were added to the emulsions II, III and B. Next  
 35 formaldehyde solutions were added to the emulsion as indicated in the following.

- 7 -

All emulsions used had a solids content of 54.6% by weight.

The coating composition were applied to a glass plate at room temperature at a thickness of 100 $\mu$ m. After evaporation of water and solvents a 20-50  $\mu$ m dry coating layer was obtained.

Figure 1 shows the hardness buildup (in terms of the number of pendulum oscillations) as a function of time (the number of days) for seven coatings based on the following compositions:

- 1) emulsion B (alkyd resin without acetoacetate groups) without formaldehyde (-AC-F)
- 2) emulsion B (alkyd resin without acetoacetate groups) with 1.6 g of 37% formaldehyde solution (-AC+F)
- 3) emulsion II (alkyd resin with 11.2% acetoacetate groups) without formaldehyde (+AC-F)
- 4) emulsion II (alkyd resin with 11.2% by weight acetoacetate groups) with 1.6 g of 37% formaldehyde solution (+AC+F)
- 5) emulsion III (alkyd resin with 5.6% by weight acetoacetate groups) without formaldehyde (0.5AC-F)
- 6) emulsion III (alkyd resin with 5.6% by weight acetoacetate groups) with 0.8 g of 37% formaldehyde solution (0.5AC+0.5F)
- 7) emulsion III (alkyd resin with 5.6% acetoacetate groups) with 1.6 g of 37% formaldehyde solution (0.5AC+F)

The hardness build-up was monitored by a measurement according to the König pendulum hardness test (DIN 53157).

These examples show that the coatings 4), 6) and 7) which are based on binder compositions comprising a polymer having acetoacetate groups and

- 8 -

formaldehyd are immediately tackfree after evaporation of water.

Furthermore, the combination of formaldehyde and an acetoacetate-functional alkyd resin in emulsion  
5 results in a more rapid hardness buildup in the first stage of the drying process.

All publications referred to herein are hereby incorporated by reference. While the invention has been described in detail and with reference to  
10 specific embodiments thereof, it will be apparent to those of ordinary skill in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

C L A I M S

1. A binder composition comprising a strongly  
activated carbanion-functional polymer and a  
crosslinker, characterized in that the crosslinker  
contains aldehyde groups and the polymer is an  
alkyd resin or a polyester resin.
2. A binder composition according to claim 1,  
characterized in that, said carbonion-functional  
groups are acetoacetate groups, malonate groups,  
acetate groups or mixtures thereof.
3. A binder composition according to claim 1,  
characterized in that the polymer is an alkyd  
resin having said carbonion-functional groups and  
having a hydroxyl number between 40 and 70 mg of  
KOH/gram of resin and an acid number between 15  
and 25 mg of KOH/gram of resin.
4. A binder composition according to any one of  
claims 1-3 characterized in that crosslinker  
contains aldehydes having (1-20) carbon atoms.
5. A binder composition according to any one of  
claims 1-4, characterized in that the crosslinker  
is formaldehyde, glutardialdehyde or a mixture  
thereof.
6. A binder composition according to any one of  
claims 1-5, characterized in that the binder  
composition is used in an aqueous emulsion.
7. A process for preparing a binder composition  
comprising the combination of steps of providing  
an alkyd resin having carbanion group, dispersing  
said alkyd resin in water to obtain an emulsion,  
and adding an aldehyde compound to said emulsion  
and wherein the emulsion has a particle size  
between 200 and 600 nm and the molar ratio of  
carbanion groups to said aldehyde groups is  
between 1:1 and 3:1.

- 10 -

8. Use of a binder composition according to any one of the claims 1-6 or of a binder composition obtained using the process according to claim 7 in the preparation of coating compositions.
- 5 9. Coating based on a binder composition according to any one of the claims 1-6 or coating based on a binder composition obtained using the process according to claim 7.
- 10 9. Wholly or partially coated substrate wherein the coating according to claim 9 is applied.

## AMENDED CLAIMS

[received by the International Bureau on 25 October 1996 (25.10.96);  
original claims 1-9 replaced by new claims 1-9 (2 pages)]

1. A binder composition comprising a strongly activated carbanion-functional polymer and a crosslinker, characterized in that the crosslinker contains aldehyde groups, the polymer is an alkyd resin or a polyester resin and the binder composition is used in an aqueous emulsion.
2. A binder composition according to claim 1, characterized in that, said carbanion-functional groups are acetoacetate groups, malonate groups, acetonate groups or mixtures thereof.
3. A binder composition according to claim 1, characterized in that the polymer is an alkyd resin having said carbanion-functional groups and having a hydroxyl number between 40 and 70 mg of KOH/gram of resin and an acid number between 15 and 25 mg of KOH/gram of resin.
4. A binder composition according to any one of claims 1-3 characterized in that crosslinker contains aldehydes having (1-20) carbon atoms.
5. A binder composition according to any one of claims 1-4, characterized in that the crosslinker is formaldehyde, glutardialdehyde or a mixture thereof.
6. A process for preparing a binder composition comprising the combination of steps of providing an alkyd resin having carbanion group, dispersing said alkyd resin in water to obtain an emulsion, and adding an aldehyde compound to said emulsion and wherein the emulsion has a particle size between 200 and 600 nm and the molar ratio of carbanion groups to said aldehyde groups is between 1:1 and 3:1.

AMENDED SHEET (ARTICLE 19)

7. Use of a binder composition according to any one of the claims 1-5 or of a binder composition obtained using the process according to claim 6 in the preparation of coating compositions.
8. Coating based on a binder composition according to any one of the claims 1-5 or coating based on a binder composition obtained using the process according to claim 6.
9. Wholly or partially coated substrate wherein the coating according to claim 8 is applied.

5

1/1

10

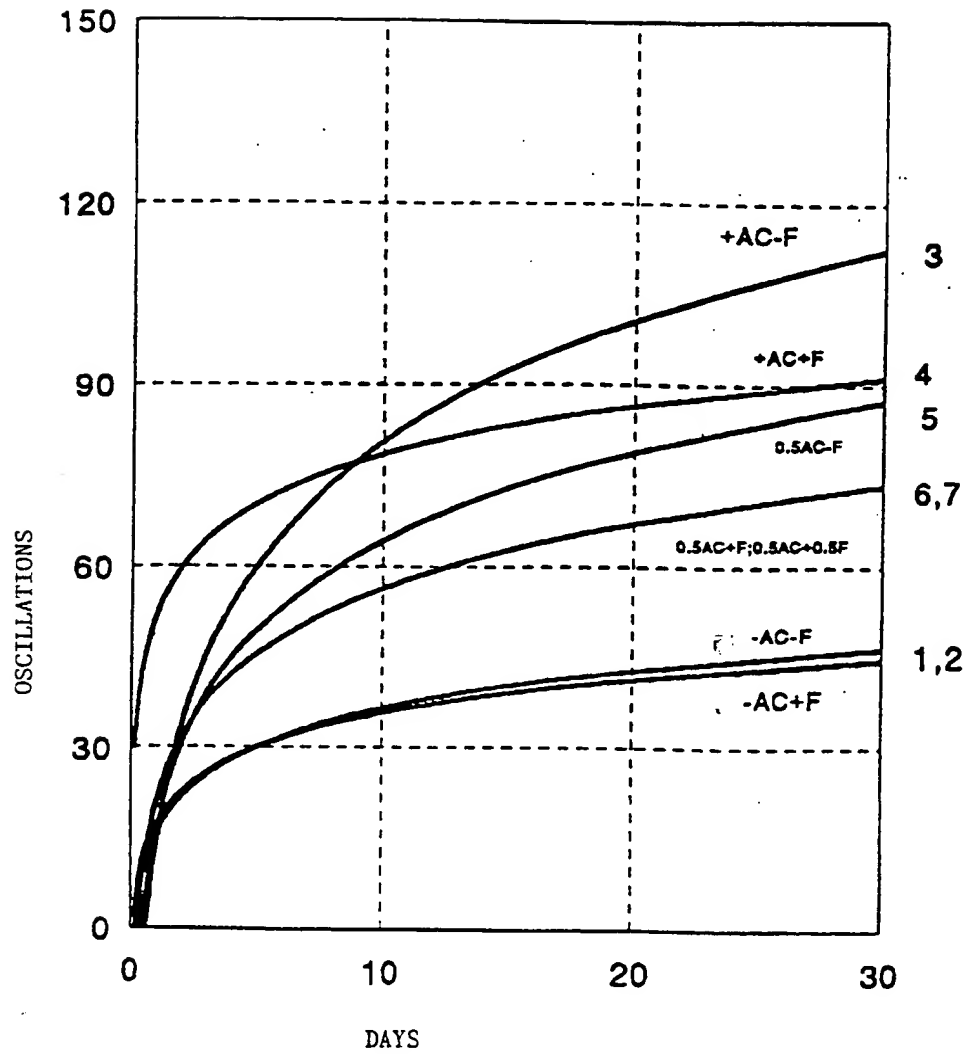
15

20

25

30

35





## INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 96/00221

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/07 C08L67/08 C08G63/91

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 213 157 (NIPPON GOHSEI) 9 August 1989 cited in the application see page 4, line 9 - line 12 see page 8, line 18 see page 15, line 16 - line 17 see claims 1,4,7; example 4; table 1 ---	1,2
A	EP,A,0 570 213 (SCOTT BADER CO.) 18 November 1993 see claims 1,2,8-10,14,15,21,18 ---	1,2,5
A	EP,A,0 227 454 (COOK PAINT) 1 July 1987 cited in the application see claims 11,12; example VI ---	1,3
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

- \* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* "&" document member of the same patent family

Date of the actual completion of the international search

4 September 1996

Date of mailing of the international search report

25.09.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Engel, S

# INTERNATIONAL SEARCH REPORT

In International Application No  
PCT/NL 96/00221

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 95, no. 012 & JP,A,07 331116 (SHINTO PAINT CO LTD), 19 December 1995, see abstract ---	1,2,4-6
X	GB,A,1 067 232 (HOECHST) 3 May 1967 see page 1, column 2, line 41 - page 2, column 1, line 40; claims 1-3,12,13; example 3 -----	1,4-6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Patent Application No

PCT/NL 96/00221

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2213157	09-08-89	JP-A- 1178566	14-07-89
		JP-B- 7057863	21-06-95
		DE-A- 3843421	13-07-89
		FR-A- 2625217	30-06-89
		US-A- 4987186	22-01-91
-----			
EP-A-570213	18-11-93	GB-A- 2268501	12-01-94
		ZA-A- 9303371	14-02-95
-----			
EP-A-227454	01-07-87	JP-A- 62223204	01-10-87
		US-A- 4804715	14-02-89
-----			
GB-A-1067232		BE-A- 651342	03-02-65
		FR-A- 1403437	02-11-65
		NL-A- 6408730	03-02-65
-----			